An unusual intermolecular interaction between a lone pair and an electron-rich π -electron system of a quinoid dianion

Vedran Vuković,^a Tomislav Piteša^b, Christian Jelsch,^a Emmanuel Wenger,^a Krešimir Molčanov^{*b}

^a CRM2, CNRS, Université de Lorraine, 54000 Nancy, France; ^b Ruđer Bošković Institute, Bijenička 54, HR-10000 Zagreb, Croatia

e-mail: kmolcano@irb.hr

KEYWORDS π -hole interactions, 2,5-dihydroxyquinone, charge density, crystal structure, DFT computations

ABSTRACT The crystal structure of lithium 2,5-dihydroxyquinonate dihydrate bis(dimethylsulfoxide) solvate [Li₂DHQ(H₂O)₂(DMSO)₂] reveals a close contact between the lone pair on the electropositive S atom of DMSO and the dianionic quinoid ring. This contact, resembling a π -hole interaction involving a dianion as an acceptor was studied in detail by a combination of X-ray charge density and quantum chemical modelling. Topology of electron density reveals a bond path and a (3, -1) critical point between the S atom of the DMSO and a C atom of the quinoid ring, while analysis of electrostatic potential indicates that the interaction between these two atoms is repulsive. However, the global electrostatic interaction between the DMSO and the dihydroxyquinonate moieties is attractive (-19.1 kJ/mol), as well as total *in vacuo* interaction energy (-42.8 kJ/mol).

INTRODUCTION

A class of intermolecular interactions, which recently came into a research focus, are those involving electron density depletions of a π -system, generally named π -hole interactions.¹⁻⁴ They typically involve electrostatic attraction of an electron-rich group with an electron-depleted region of a π -electron system.³⁻⁶ Donation of a lone electron pair (lp) into an empty π^* orbital of the π -system (i.e. lone pair $\cdots\pi$ or $n\rightarrow\pi^*$ interactions) explains some cases of π -hole interactions.^{4,7-9} Anions also form anion $\cdots\pi$ interactions with electron-depleted conjugated rings.^{2,10-14}

Formation of anion $\cdots\pi$, lp $\cdots\pi$ and $n\rightarrow\pi^*$ interaction necessitates the presence of a positive electrostatic potential (ESP) zone in a conjugated system (i.e. a π -hole) on the acceptor. Commonly used acceptors include aromatic rings with multiple electron-withdrawing substituents; non-aromatic perhalogenoquinones have been investigated recently.¹⁵⁻¹⁷ Generally, quinoid rings are inherently electron-poor due to the presence of strongly electron-withdrawing carbonyl groups. Their influence is exacerbated by the π electrons which are much more localised than in the aromatics (*i.e.* single and double bonds in quinones can be easily distinguished¹⁸). Electronegative substituents such as halogens further deplete the electron density of quinoid rings, resulting in very pronounced π -holes located at carbonyl C atoms.^{15,19-21} Intermolecular contacts shorter than the sum of van der Waals radii were observed between perhalogenquinones and halide anions.¹⁵⁻¹⁷

So far, only severely electron-depleted π systems were considered as possible acceptors of π -hole interactions. In this paper, we present a detailed study of a serendipitously obtained compound with a contact resembling a lone pair $\cdots\pi$ interaction involving an electron-rich dianionic quinonid ring 2,5-dihydroxyquinonate (**DHQ**). To reveal more details on the nature of this counterintuitive interaction, we have studied it by a combination of experimental X-ray charge density and quantum chemical modelling.

Scheme 1 Lewis structural formula and atom numeration scheme of $\text{Li}_2\text{DHQ}(\text{H}_2\text{O})_2(\text{DMSO})_2$ (**1**).

RESULTS AND DISCUSSION

The studied compound, lithium 2,5-dihydroxyquinonate dihydrate bis(dimethylsulfoxide) solvate [$\text{Li}_2\text{DHQ}(\text{H}_2\text{O})_2(\text{DMSO})_2$], **1**, Scheme 1] was serendipitously obtained by recrystallization of lithium 2,5-dihydroxyquinonate [22] in dimethylsulfoxide (DMSO). Asymmetric unit of the compound comprises a half of a **DHQ** dianion, a lithium cation, a water molecule and a molecule of DMSO.

Structure of the 2,5-DHQ dianion: induction effect of substituents quantified by analysis of charge density

Bond lengths in the **DHQ** dianion (Table S3) is in a good agreement with its other alkali salts,²³ confirming the structure shown in Scheme 1. Several substituted 2,5-dihydroxyquinones also have two delocalised π systems separated by two single C-C bonds: 3,6-dichloro analogue (chloranilate dianion, **CA**),^{18,24-26} 3,6-dibromo analogue (bromanilate dianion, **BA**),²⁷ 3,6-dinitro analogue (nitranilate dianion, **NA**)^{28,29} and 3-cyano-6-chloro analogue.³⁰

Experimentally determined charge density for chloranilate¹⁸ and nitranilate dianions²⁸ can be compared to **DHQ** to quantify substituent inductive effect. Electron-withdrawing substituents enhance negative charge delocalisation and thus increase hydroxyl group acidity.^{24,30} Their effect on molecular geometry is negligible. Bond orders calculated from electron density show a clear trend (Table 1): electron density in the carbon ring is reduced as electron-withdrawing power of the substituents increases. This effect is the most pronounced for the delocalised bonds C2-C3 and

C3-C1ⁱ, whose estimated bond order decreases from 1.43 in **DHQ** to 1.25 in **CA**¹⁸ and to less than 1.0 in **NA**.²⁸ Order of the formally single bond C1-C2 decreases from 0.77 in **DHQ** to 0.67 in **NA**.²⁸ Electron-withdrawing substituents seem not to have an effect on C-O bonds. ESP maps also reveal the decrease of electron density in the carbon skeleton (Fig. 1), while Table S2 shows an increase of negative charges on substituents.

The distribution of charges on dihydroxyquinonate ion (Tables S1 and S2) is comparable to that of chloranilate^{18,31} and the nitrilate anion.²⁸ The oxygen atoms are more negative, while the hydrogen is more positive than comparable substituents in other quinones. It appears as if the electron density from these hydrogen atoms re-locates to the oxygen atoms on the edges of π -systems.

Table 1 Comparison of bond orders in the quinoid dianions **DHQ**, **CA**¹⁸ and **NA**.²⁸

Bond	DHQ	CA	NA
C1-C2	0.77	0.76	0.67
C2-C3	1.45	1.25	0.90
C3-C1 ⁱ	1.41	1.25	0.76
C1-O1	1.34	1.48	1.47
C2-O2	1.30	1.45	1.37

Symmetry operator: *i*) $-x, -y, -z$.

Figure 1 Comparison of electrostatic potentials plotted onto an electron density isosurface of $0.5 \text{ e } \text{\AA}^{-3}$ generated by the **DHQ**, **CA**¹⁸ and **NA**²⁸ quinoid dianions.

*Interaction between a lone pair of DMSO and a π -system of **DHQ** dianion*

The basic building block of the crystal structure of **1** is a centrosymmetric moiety $\text{Li}_2\text{DHQ}(\text{H}_2\text{O})_2(\text{DMSO})_2$, with the **DHQ** ring centroid located at the crystallographic inversion centre (Scheme 1, Figure S6). The lithium cation has a tetrahedral coordination by O1 and O2 atoms from **DHQ**, water molecule oxygen O4, and DMSO oxygen O3. There are two symmetry-independent O-H $\cdots$ O hydrogen bonds and seven weaker C-H $\cdots$ O, which form layers parallel to ($\bar{1}01$) (Fig. 2) containing alternatively (**DHQ**, H_2O , Li^+) and DMSO moieties. Therefore, there is no π -stacking of **DHQ** rings in the crystal structure.

A close contact between the DMSO sulphur atom and the **DHQ** ring stands apart as the most interesting feature in the crystal structure (Fig. 3). The closest separation is S1 $\cdots$ C2 of 3.2481(7) Å, followed by S1 $\cdots$ C1 of 3.4046(7) Å; the distance between S1 and the centre of gravity of **DHQ** ring is 3.461 Å. The molecules arrange so that the lone electron pair of S1 points towards the π -system of the quinoid ring (Fig. 3). The interaction between a **DHQ** dianion and a lone pair is not expected to be electrostatically attractive: electrostatic potential at atoms C1 and C2 is higher than the rest of the ring, but still negative (Figs. 1 and 4).

The ESP generated by **DHQ** on the Hirshfeld surface of the " π -hole" (at atom C2) is -0.55 V , while the DMSO ESP at the position of the sulphur lone pair it is -0.05 V . Despite the local

electron-depletion of atom C2, the ESP in its surroundings is negative, due to the global charge of **DHQ** dianion potential. Moreover, the q_{model} atomic charge derived from P_{val} is +0.41 e for S1, while on the **DHQ** side it is 0.00 e for C1 and +0.01 e for C2, meaning that these atoms are richer in electrons than the S1 sulphur (Fig. 5). From an electrostatic point of view, this interaction shouldn't be attractive.

The new *Charger* electrostatic interaction energy tool³² expands this simple charge-based analysis. It considers the full charge density description around selected pseudo-atoms. Both S1...C1 and S1...C2 electrostatic interaction energies are slightly positive (+0.9 and +2.5 kJ/mol, respectively): the pseudo-atoms in direct contact repulse each other electrostatically. However, the interaction becomes attractive when the S1=O3 group is considered instead of just the S1 atom: respective electrostatic energies of the contacts (O3=S1)...C1 and (O3=S1)...C2 become -0.5 and -1.2 kJ/mol. Presumably the electrostatic repulsion between S and C is compensated by the electronegative oxygen. This occurs often with the multipolar model, in which the ensemble of the two pseudo-atoms that form a covalent bond describe its density. However, the electrostatic energies between S1 and the two C3 atoms in the quinoid ring, with respective distances of 3.6386(7) and 3.8371(7) Å are -36.2 and -32.8 kJ/mol. This attractive energy is mostly contributed by the deformation energy -37.9 and -35.7 kJ/mol (0.03 e Å⁻³), which originates from the $N_{\text{val}}-P_{\text{val}}$ charges S1 (+0.41e) and C3 (-0.24e). The overall **DHQ**...DMSO interaction energy (-19.1 kJ/mol) indicates a strong global electrostatic attraction between them.

The topology of electron density revealed multiple bonding critical points (cp, Table 2, Fig. 6). The strongest ones correspond to O-H...O hydrogen bonds, followed by S1...C2 contact (electron density at the cp is 0.056 eÅ⁻³), while C-H...O hydrogen bonds are considerably weaker. However, the presence of (3, -1) critical points does not always imply the existence of attractive interactions,^{33,34} especially in the case of weak intermolecular interactions.³⁵ The S1...C2 atom contact is not attractive from a pure electrostatic point of view, but is the result of the global attraction between the **DHQ** and DMSO entities.

However, quantum-chemical *in vacuo* computations, employing density functional theory, tell a different story. First, geometry optimization of **DHQ**²⁻...DMSO complex *in vacuo*, starting from the geometry as found in crystal structure of **1**, did not yield a complex with either S...C or S...O interaction, but rather a C-H...O hydrogen-bonded complex. Nevertheless, total (electronic, not electrostatic) energy of interaction between **DHQ**²⁻ and DMSO at the crystal-structure geometry

of $\text{DHQ}^{2-} \cdots \text{DMSO}$ appears strongly attractive (-42.8 kJ/mol). To investigate further the nature of this interaction, we analysed the electron density difference (EDD) upon formation of the interaction (Fig. 7). This analysis shows that the interaction shifts electron density from the lone-pair region of S1 closer to its nucleus and to the O1 of DHQ^{2-} . Investigation of the $\text{N-Br} \cdots \text{N}$ halogen bond has shown analogous EDD behaviour (sigma-hole of bromine loses the density upon halogen bond formation), so the total interaction might also include a chalcogen-like component. However, it is more likely that the electron depletion of S1 is a result of a close contact with the dianion. Such result is surprising since geometry of the $\text{S1} \cdots \text{O2}$ contact is not favourable ($\text{O3=S} \cdots \text{O2}$ angle is 139.4°) for formation of chalcogen interaction and also $(3, -1)$ critical point is experimentally found between S1 and C2, rather than between S1 and O2.

Figure 2 Crystallographic autostereogram of **I** viewed approximately normal to the $(\bar{1}01)$ plane. The $\text{H-O-H} \cdots \text{O-C}$ hydrogen bonds are shown as dotted lines.

Figure 3 Close contact between DMSO and **DHQ** dianion. The lone pair of the S1 atom (shown in blue) is directed approximately towards the ring centroid (shown as red sphere); contact S...C is shown as red dashed line.

Figure 4. Deformation electron density map of the **DHQ** dianion. Contours: blue: $+0.25\text{e}/\text{\AA}^3$, red: $-0.125\text{ e}/\text{\AA}^3$.

Figure 5 Electrostatic potential of a DMSO molecule plotted onto an electron density isosurface of a) 0.5 e Å⁻³ and b) 0.005 e Å⁻³.

Table 2 Total electron density ρ_{tot} and Laplacian $\nabla^2\rho$ at the intermolecular contacts (critical points of the (3, −1) type between molecules) in **I**. Experimentally determined cp's are printed regular and theoretical ones are in italic.

$A\cdots B$	$d / \text{\AA}$	$\rho_{\text{tot}} / \text{e \AA}^{-3}$		$\nabla^2\rho / \text{e \AA}^{-5}$		$G_{\text{cp}} / \text{e \AA}^{-3}$		$V_{\text{cp}} / \text{e \AA}^{-3}$		$ V_{\text{cp}} / G_{\text{cp}}$	
		exp.	theor.	exp.	theor.	exp.	theor.	exp.	theor.	exp.	theor.
S1 $\cdots$ C2 ⁱ	3.248(7)	0.056	<i>0.063</i>	0.68	<i>0.76</i>	0.006	<i>0.006</i>	−0.004	<i>−0.005</i>	0.67	<i>0.83</i>
H1WA $\cdots$ O1 ⁱⁱ	1.766(6)	0.308	<i>0.231</i>	2.34	<i>1.55</i>	0.033	<i>0.021</i>	−0.042	<i>−0.026</i>	1.27	<i>1.24</i>
H1WB $\cdots$ O2 ⁱⁱⁱ	1.739(6)	0.337	<i>0.258</i>	2.41	<i>1.45</i>	0.036	<i>0.022</i>	−0.047	<i>−0.030</i>	1.31	<i>1.36</i>
H3 $\cdots$ O3 ^{iv}	2.963(7)	0.013	<i>0.018</i>	0.24	<i>0.25</i>	0.002	<i>0.002</i>	−0.001	<i>−0.001</i>	0.50	<i>0.50</i>
H4A $\cdots$ O1W ^v	2.859(8)	0.020	<i>0.028</i>	0.33	<i>0.31</i>	0.002	<i>0.002</i>	−0.001	<i>−0.002</i>	0.50	<i>1.00</i>
H4B $\cdots$ O3 ^{vi}	2.464(6)	0.043	<i>0.072</i>	0.84	<i>0.60</i>	0.006	<i>0.006</i>	−0.004	<i>−0.005</i>	0.67	<i>0.83</i>
H4C $\cdots$ O1 ^{vii}	2.674(6)	0.031	<i>0.040</i>	0.51	<i>0.43</i>	0.004	<i>0.004</i>	−0.002	<i>−0.003</i>	0.50	<i>0.75</i>
H5A $\cdots$ O1W ^v	2.649(8)	0.029	<i>0.045</i>	0.54	<i>0.48</i>	0.004	<i>0.004</i>	−0.002	<i>−0.003</i>	0.50	<i>0.75</i>
H5B $\cdots$ O2 ^{viii}	2.524(9)	0.050	<i>0.060</i>	0.79	<i>0.74</i>	0.006	<i>0.01</i>	−0.005	<i>−0.01</i>	0.83	<i>0.83</i>
H5C $\cdots$ O3 ^{viii}	2.671(10)	0.037	<i>0.033</i>	0.56	<i>0.45</i>	0.004	<i>0.004</i>	−0.003	<i>−0.002</i>	0.75	<i>0.50</i>

Symmetry operation on B: (i) $^{3/2-x, 1/2+y, 1/2-z}$; (ii) $1-x, 2-y, 1-z$; (iii) $^{-1/2+x, 3/2-y, -1/2+z}$; (iv) $^{1/2+x, 3/2-y, 1/2+z}$; (v) $^{1/2+x, 3/2-y, -1/2+z}$; (vi) $1-x, 2-y, -z$; (vii) $1-x, 1-y, 1-z$; (viii) $^{3/2-x, -1/2+y, 1/2-z}$.

Figure 6 Critical points in a $\text{Li}_2\text{DHQ}(\text{H}_2\text{O})_2(\text{DMSO})_2\cdot\text{DMSO}$ moiety. $(3,-1)$ cp's are shown as blue spheres, $(3,+1)$ ring CPs as green spheres and bond paths are shown as blue lines.

Figure 7 Isosurface of theoretical electron density difference (EDD) upon formation of **DHQ²⁻...DMSO** interaction, $\Delta\rho = \rho(\text{DHQ}^{2-}\cdots\text{DMSO}) - \rho(\text{DHQ}^{2-}) - \rho(\text{DMSO})$, for isovalue ± 0.0007 a.u. (brown – negative isovalue, blue – positive isovalue).

CONCLUSIONS

The crystal structure of $\text{Li}_2\text{DHQ}(\text{H}_2\text{O})_2(\text{DMSO})_2$ (**1**) comprises an unusual intermolecular contact resembling a π -hole interaction involving a dianion as an acceptor. A detailed study of the close contact between the sulphur atom of DMSO and the **DHQ** dianion by a combination of X-ray charge density and quantum chemical modelling was undertaken to study nature of this unusual interaction.

The topology analysis indicates the presence of a critical point, but the analysis of the ESP tells that the interaction is not localised, and the electrostatic interaction between pseudoatoms S1 and

C2 is in fact repulsive. On the contrary, when taking into account the entire DMSO molecule and a **DHQ** dianion, the electrostatic interaction between these two moieties becomes attractive, the total estimated energy being -19.1 kJ/mol. DFT *in vacuo* computations indicate a possible chalcogen bonding component (between S1 and carbonyl O2 atoms), and analysis of ESP indicates strong electrostatic attraction between $S1^{\delta+}$ and $C3^{\delta-}$ atoms. Therefore, we conclude that there is no local attraction between S1 and C2 atoms (despite presence of a bonding cp), but that the total interaction between a **DHQ** dianion and a molecule of DMSO is attractive. Its main component is electrostatic, but possibly involves a minor component of a chalcogen-like interaction between S1 and O2 atoms. Thus, presence of a bonding cp between S1 and C2 is a result of a generally attractive interaction between **DHQ** and DMSO as well as a combination of other interactions present in the crystal field.

This work shows that a short intermolecular contact *and* a presence of a bonding cp does not always characterise an attractive interaction. Therefore, a care should be taken when interpreting novel and apparently counterintuitive interactions.

In addition, we have quantified induction effect of substituents on electron density in the quinoid ring. A comparison of electron density in **DHQ**, **CA**¹⁸ and **NA**²⁸ dianions revealed a different distribution of ESP. Carbon-carbon bond orders in the quinoid ring decrease as electron-withdrawing capability of substituents increases.

EXPERIMENTAL

Preparation

Diaquabis(dimethylsulfoxyde)- μ -(2,5-dihydroxyquinonato)dilithium ($[Li_2\{\mu-(C_6H_2O_4)\}(H_2O)_2\{(CH_3)_2SO\}_2]$ (**I**), Scheme 1) crystals synthesis involves two steps. The first entails the neutralisation of a 2,5-dihydroxyquinone solution with an equimolar amount of lithium carbonate, forming lithium 2,5-dihydroxyquinonate, as described previously [23,36]. 2,5-dihydroxyquinonate crystalizes by evaporation of this solution in air. The crystals were not large enough for a high-resolution diffraction experiment. They were then re-crystallised from a dimethylsulfoxyde solution. Well-developed crystals of $[Li_2\{\mu-(C_6H_2O_4)\}(H_2O)_2\{(CH_3)_2SO\}_2]$ (**I**) grew over the course of six months at room temperature.

X-ray diffraction and multipolar refinement

Collection of diffraction data. The diffraction data for a single crystal of **1** were collected using a Bruker D8 Venture diffractometer equipped with a molybdenum micro-focus X-ray tube with a mirror monochromator, and a PHOTON 100 CMOS detector. MoK α radiation ($\lambda = 0.71073$ Å) was used. Bruker SAINT software performed data reduction and numerical absorption correction based on crystal shape.³⁷ The full dataset contains 97590 reflections up to the resolution of $\sin(\theta)/\lambda = 1.0$ Å⁻¹, 6889 of which are symmetry-independent. The data set is 99.7% complete, with $R_{\text{int}} = 7.06\%$; detailed statistics can be found in Table 3.

Table 3 Details and statistics about gathered crystallographic data, as well as structure and charge density refinement of **1**.

Compound	1
Empirical formula	C ₅ H ₆ ClLiSO ₄
Empirical mass / (g/mol)	209.56
Crystal dimensions / mm ³	451 x 336 x 132
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	8.1521(7)
<i>b</i> / Å	8.9827(7)
<i>c</i> / Å	11.1947(9)
α / °	90
β / °	93.238(4)
γ / °	90
<i>Z</i>	4
<i>V</i> / Å ³	818.46(12)
<i>D</i> _{calc} / (g/cm ³)	1.397

μ / mm^{-1}	0.355
Θ range / $^{\circ}$	2.91 – 45.42
T / K	100(2)
$\lambda / \text{\AA}$	0.71073
Diffractometer type	Bruker D8 Venture
h, k, l range	$-16 < h < 15$ $-17 < k < 17$ $-22 < l < 22$
Resolution / $\text{\AA}$	0.500
Reciprocal resolution / $\text{\AA}^{-1}$	1.000
Gathered reflections	97 590
Independent reflections	6889
Reflections with $I \geq 2\sigma$	4871
Absorption correction	Multi-scan
T_{min}	0.856
T_{max}	0.955
Statistical weighting scheme	$\{1.06 \sigma^2(F_{\text{obs}})\}^{-1}$
Completeness (%)	99.7
R_{int} (%)	7.06
$R(F)$ (%)	5.007
$R(F^2)$ (%)	3.307
Goodness-of-fit	1.003

Number of parameters	304
Number of constraints/restraints	143
$\Delta\rho_{\min} / \text{e } \text{\AA}^{-3}$	−0.44
$\Delta\rho_{\max} / \text{e } \text{\AA}^{-3}$	0.46

Structure solution and initial spherical refinement. The Olex2 graphical user interface served to solve and refine the structure of **1**.³⁸ To this end, it employed exterior programs SHELXS97³⁹ and SHELXL-2017.⁴⁰ The structures were refined using the least-squares method. Anisotropic displacement parameters were used for all atoms, except hydrogens. Hydrogen atoms were found from difference Fourier maps and refined without restraints. Molecular graphics were made using CCDC-Mercury⁴¹ and POV-Ray.⁴²

Charge density refinement. The program Import2MoPro from the MoProSuite transformed the solved and refined crystal structure of **1** into the appropriate format for further refinement.⁴³ SORTAV removed symmetry-forbidden reflections and averaged the remaining ones.⁴⁴

The program MoPro refined the crystal structure using the Hansen-Coppens multipolar model.⁴³ A gradual refinement of following parameters was executed: scaling factor coefficients, atomic coordinates, anisotropic displacement parameters, valence populations, multipolar coefficients (none for lithium atoms; up to dipolar level for hydrogen atoms; octupolar levels for carbon and oxygen atoms; hexadecapolar level for the sulphur atom), and expansion/contraction parameters κ and κ' . The least-squares refinement had the goal of minimising the difference between observed (I_{obs}) and calculated intensities (I_{calc}).

A quantum-chemistry calculation on the SHADE3 server determined anisotropic displacement parameters of hydrogen atoms from 2,5-dihydroxyquinonate dianion and dimethylsulfoxide.^{45,46} Calculated values of $U_{\text{ani}}(\text{H})$ were constrained to those from SHADE3 during the refinement. There was insufficient data to determine $U_{\text{ani}}(\text{H})$ for the water molecule because the program SHADE3 requires at least four non-hydrogen atoms be present in the molecule.

Restraints on X–H bond lengths were as follows: 0.983(2) Å for O–H bonds in water, 1.083(2) Å for C–H bonds in 2,5-dihydroxyquinonate ion and 1.077(2) Å for C–H bonds in methyl groups

of DMSO.⁴⁷ Furthermore, dipolar, quadrupolar and expansion/contraction parameters for the water molecule were constrained to those from the ELMAM2 database.⁴⁸

Several $R_{F,\text{free}}$ and $wR^2_{F,\text{free}}$ calculations with 20 refinement cycles determined optimal restraint values for multipolar local symmetry and valence/multipolar population similarities. The minimum of $R_{F,\text{free}}$ and $wR^2_{F,\text{free}}$ curves was the basis to determine optimal restraint values.

We used three graphical techniques to evaluate model quality: the DR plot (values of $(I_{\text{obs}} - I_{\text{calc}}) / \sigma(I_{\text{obs}})$ vs. theoretical quantiles of a standard normal distribution; the points should be on the $y=x$ line),^{49,50} the resolution plot (values of $I_{\text{obs}}/I_{\text{calc}}$ vs. reciprocal resolution $\sin(\Theta) / \lambda$; the points should be on the $y=1$ line),⁵⁰ and the fractal dimension plot (value of residual density at different iso-surfaces vs. fractal dimension of those iso-surfaces; the points should form a parabola with the maximum at (0, 3) in case of purely Gaussian noise). The first two plots were made with XDRKplots, and the third with jnk2RDA.^{51,52}

The ground to decide in which directions to proceed with the refinement was the compromise between improving these plots, residual density global minimum/maximum values and deformation density contour plots. In the final cycles of refinement, the resolution of diffraction data used for refinement was limited to $\sin(\Theta) / \lambda = 0.95 \text{ \AA}^{-1}$ due to $I_{\text{obs}}/I_{\text{calc}}$ scaling deviating to values higher than unity at higher resolution (Fig. S1).

Charge density analysis. *VMoPro* calculated total charge density cubes for the entire complex (two asymmetric units related by inversion in the centre of the quinone ring). *VMoPro* further calculated ESPs, bond critical points and their parameters (density, eccentricity, density Laplacian etc.).⁴³

Atomic charges were calculated in two ways. The first is directly from the Hansen-Coppens model, which contains the parameter of valence population P_{val} . This charge is hence called the model charge, calculated as the difference between neutral and modelled valence populations: $q_{\text{model}} = N_{\text{val}} - P_{\text{val}}$. The second way to calculate charges is an integration of charge density in the volume of the space designated to each atom. The program *Critic2* calculated topological charges using the Bader partitioning method (q_{Bader}) from total charge density cubes.⁵³

Topological bond orders were determined using an empirical formula:

$$n_{\text{topo}} = a + b \lambda_1 + c (\lambda_2 + \lambda_3) + f \rho_{\text{cp}}.$$

The values a , b , c and f are empirical parameters taken from literature sources,⁵⁴⁻⁵⁶ ρ_{cp} represents the charge density at the critical point, and λ_1 , λ_2 and λ_3 represent density Hessian values at the critical point ($\lambda_1 \geq \lambda_2 \geq \lambda_3$).

MoProViewer created visual representations of molecules with charge density surfaces.⁵⁷ *VMoPro* generated most two-dimensional property plots. For standard deviation plots, *MoProViewer* 2D slices from 3D cubes functionality were applied.⁵⁷

The calculation of standard deviations for all these parameters required several tools. *MoPro* can generate structures with errors added to all parameters (from the atomic coordinates to the multipolar coefficients).⁵⁸ These errors are taken from the standard normal distribution and transformed to random deviations appropriate for each individual parameter (coming from the variance-covariance matrix during crystallographic refinement).

Twenty structures with errors generated in this way enable calculations of standard deviations for model parameters and derived properties.

All these structures were processed as described above (charge density 3D cubes calculation, critical point analysis, topological charge integration, topological bond order determination). Three-dimensional cubes of charge density standard deviations were calculated in the “3D map operations” module of *MoProViewer*.⁵⁷ Critical point parameters and topological charges were loaded into a Jupyter-Notebook-enabled⁵⁹ Python script⁶⁰ which calculated their standard deviations using the *Pandas* module.⁶¹ Additionally, it estimated topological bond orders according to the formula above, and their standard deviations.

Quantum chemical computations

Atomic coordinates after multipolar refinement were converted with *MoPro* into an input file for the quantum chemistry program *Crystal14*^{62,63}. This program was used to calculate periodical wave-function without prior geometry optimisation of initial crystal structures. Periodic DFT using the B3LYP functional was used to determine the adequate wave-function which describes the crystal. Basis sets of functions for carbon,⁶⁴ hydrogen,⁶⁴ oxygen⁶⁴ and sulphur⁶⁵ atoms were of 6-31G(d,p) type, adapted for periodical calculations according to recommendations from literature. The adaptations were not found for lithium atoms, so the 6-31G(d,p) non-periodic coefficients were used.⁶⁶

The amount of available memory for integral calculation was increased to ensure their correctness. Tolerance boundaries for two-electron integrals during orbital pseudo-overlap were increased according to recommendations from literature.⁶⁵ Self-consistent bond-perturbed Kohn-Sham matrix calculation was interrupted after 100 cycles maximum. Kohn-Sham matrix eigenvalues are reduced by 0.6 hartree to improve wave-function convergence.⁶³

The program *properties* derived structural factors up to $\sin(\Theta) / \lambda = 1.28 \text{ \AA}^{-1}$ resolution from the calculated wave-function.^{62,63} Calculated structure factors were used with experimentally-determined atomic coordinates to refine a Hansen-Coppens charge density using *MoPro*. The following parameters were gradually refined: valence populations, multipolar coefficients (like in the experimental model, except for hydrogen atoms where quadrupolar parameters were also refined) and the values of parameters κ and κ' . Charge densities were refined with the least-squares method, by minimising the difference of observed (F_{obs}) and calculated structural factors (F_{calc}).

Physically non-justifiable κ and κ' values in experimentally determined charge densities were restrained to parameters obtained from this theoretical model. Lithium and sulphur atoms had problems with κ values, so the refinement had them restrained to 0.997(10) and 1.002(10) respectively. Similarly, κ' values of oxygen atoms had to be restrained to 0.907(10) for O1, 0.999(10) for O2 and 1.098(10) for O3.

In vacuo DFT calculations were performed with the Gaussian 09 program.⁶⁷ Geometry optimizations were performed on the B3-LYP⁶⁸ /jun-cc-pVTZ⁶⁹ level of theory with Grimme's D3 dispersion correction,⁷⁰ starting from the crystal-structure geometries of DHQ...DMSO and $\text{Li}_2(\text{H}_2\text{O})_2\text{DHQ}(\text{DMSO})_2$ moiety. The calculation of interaction energy was performed on the crystal-structure geometry of $\text{DHQ}^2\cdots\text{DMSO}$ complex on the same level of theory and with counterpoise scheme of Boys and Bernardi to account for the BSSE.⁷¹ The EDD calculation was performed on the CAM-B3LYP⁷² /jun-cc-pVTZ level on the crystal-structure geometry of $\text{DHQ}^2\cdots\text{DMSO}$.

ASSOCIATED CONTENT

Supporting Information. Additional details on refinement an electron density; molecular geometry; atomic charges and electrostatic potential. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

* Krešimir Molčanov, Ruđer Bošković Institute, Bijenička 54, HR-10000 Zagreb, Croatia, e-mail kmolcano@irb.hr

Present Addresses

†If an author's address is different than the one given in the affiliation line, this information may be included here.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

The Croatian Science Foundation financed this work, via its grant no. IP-2019-04-4674. V.V. is thankful for the French PhD fellowship of MENSRT.

ACKNOWLEDGMENT

We thank the X-ray diffraction facility PMD²X of the Institut Jean Barriol, Université de Lorraine, for X-ray diffraction measurements. (<http://crm2.univ-lorraine.fr/lab/fr/services/pmd2x>)

ABBREVIATIONS

DHQ, 2,5-dihydroxyquinonate dianion; CA, chloranilate dianion; BA, bromanilate dianion; NA, nitranilate dianion; DMSO, dimethylsulfoxide; EDD, electron density difference; cp critical point; ESP, electrostatic potential

REFERENCES

[1] Quiñonero, D.; Garau, C.; Rotger, C.; Frontera, A.; Ballester, P.; Costa, A.; Deya, P. M. Anion- π Interactions: Do They Exist? *Angew. Chem. Int. Ed.* **2002**, 41, 3389–3392.

[2] Frontera, A.; Gamez, P.; Mascal, M.; Mooibroek, T. J.; Reedijk, J. Putting Anion- π Interactions Into Perspective. *Angew. Chem. Int. Ed.* **2011**, 50, 9564–9583.

[3] Kozuch, S. Should “anion- π interactions” be called “anion- σ interactions”? A revision of the origin of some hole-bonds and their nomenclature. *Phys. Chem. Chem. Phys.* **2016**, 18, 30366–30369.

[4] Angarov, V.; Kozuch, S. On the σ , π and δ hole interactions: a molecular orbital overview. *New. J. Chem.* **2018**, 42, 1413–1422.

[5] Grounds, O.; Zeller, M.; Rosokha, S. V. Structural preferences in strong anion- π and halogen-bonded complexes: π - and σ -holes vs. frontier orbitals interaction. *New J. Chem.* **2018**, 42, 10572–10583.

[6] Jia, C.; Miao, H.; Hay, B. P. Crystal Structure Evidence for the Directionality of Lone Pair- π interactions: Fact or Fiction? *Cryst. Growth Des.* **2019**, 19, 6806–6821.

[7] Mooibroek, T. J.; Gamez, P.; Reedijk, J. Lone pair- π interactions: a new supramolecular bond? *CrystEngComm* **2008**, 10, 1501–1515.

[8] Sing, S. K.; Das, A. The $n \rightarrow \pi^*$ interaction: a rapidly emerging non-covalent interaction. *Phys. Chem. Chem. Phys.* **2015**, 17, 9596–9612.

[9] Newberry, R. W.; Raines, R. T. The $n \rightarrow \pi^*$ Interaction. *Acc. Chem. Res.* **2017**, 50, 1838–1846.

[10] Schottel, B. L.; Chifotides, H. T. Dunbar, K. R. Anion- π interactions. *Chem. Soc. Rev.* **2008**, 37, 68–83.

[11] Gamez, P.; Mooibroek, T. J.; Teat, S. J.; Reedijk, J. Anion Binding Involving π -Acidic Heteroaromatic Rings. *Acc. Chem. Res.* **2007**, 40, 435–444.

[12] Wang, D.-X.; Wang, M.-X. Anion- π Interactions: Generality, Binding Strength, and Structure. *J. Am. Chem. Soc.* **2013**, 135, 892–897.

[13] Lucas, X.; Bauzá, A.; Frontera, A.; Quiñonero, D. A thorough anion- π interaction study in biomolecules: on the importance of cooperativity effects. *Chem. Sci.* **2016**, 7, 1038–1050.

- [14] Savastano, M.; Bazzicalupi, C.; García, C.; Gellini, C.; Lopez de la Torre, M. D.; Mariani, P.; Pinchierri, F.; Bianchi, A.; Melguizo, M. Iodide and triiodide anion complexes involving anion- π interactions with a tetrazine-based receptor. *Dalton Trans.* **2017**, 46, 4518–4529.
- [15] Molčanov, K.; Mali, G.; Grdadolnik, J.; Stare, J.; Stilinović, V.; Kojić-Prodić, B. Iodide $\cdots\pi$ interactions of perhalogenated quinoid rings in co-crystals with organic bases. *Cryst. Growth Des.* **2018**, 18, 5182–5193.
- [16] Kepler, S.; Zeller, M.; Rosokha, S. V. Anion- π Complexes of Halides with p-Benzoquinones: Structures, Thermodynamics, and Criteria of Charge Transfer to Electron Transfer Transition. *J. Am. Chem. Soc.* **2019**, 141, 9338–9348.
- [17] Wilson, J.; Maxson, T.; Wright, I.; Zeller, M.; Rosokha, S. V. Diversity and uniformity in anion- π complexes of thiocyanate with aromatic, olefinic and quinoidal π -acceptors. *Dalton Trans.* **2020**, 49, 8734–8743, DOI: 10.1039/d0dt01654c.
- [18] Vuković, V.; Molčanov, K.; Jelsch, C.; Wenger, E.; Krawczuk, A.; Jurić, M.; Androš Dubraja, L.; Kojić-Prodić, B. Malleable Electronic Structure of Chloranilic Acid and Its Species Determined by X-ray Charge Density Studies. *Cryst. Growth Des.* **2019**, 19, 2802–2810.
- [19] Molčanov, K.; Jelsch, C.; Landeros, B.; Hernandez-Trujillo, J.; Wenger, E.; Stilinović, V.; Kojić-Prodić, B.; Escudero-Adan, E. Partially covalent two-electron/multicentric bonding between semiquinone radicals. *Cryst. Growth Des.* **2019**, 19, 391–402.
- [20] Molčanov, K.; Milašinović, V.; Kojić-Prodić, B. Contribution of different crystal packing forces in π -stacking: from non-covalent to covalent multicentric bonding. *Cryst. Growth Des.* **2019**, 19, 5967–5980.
- [21] Molčanov, K.; Kojić-Prodić, B. Towards understanding of π -stacking interactions of non-aromatic rings. *IUCrJ* **2019**, 6, 156–165.
- [22] Molčanov, K.; Kojić-Prodić, B.; Meden, A. π -Stacking of quinoid rings in crystals of alkali diaqua hydrogen chloranilates. *CrystEngComm* **2009**, 11, 1407–1415.

[23] Molčanov, K.; Kojić-Prodić, B.; Babić, D.; Stare, J. Face-to-face stacking of dianionic quinoid rings in crystals of alkali salts of 2,5-dihydroxyquinone in view of π -system polarization. *CrystEngComm* **2013**, 15, 135–143.

[24] Molčanov, K.; Kojić-Prodić, B.; Meden, A. Unique electronic and structural properties of 1,4-benzoquinones: crystallochemistry of alkali chloranilate hydrates. *Croat. Chem. Acta* **2009**, 82, 387–396.

[25] Molčanov, K.; Kojić-Prodić, B. Salts and cocrystals of chloranilic acid with organic bases: is it possible to predict a salt formation? *CrystEngComm* **2010**, 12, 925–939.

[26] Molčanov, K.; Sabljic, I.; Kojić-Prodić, B. Face-to-face π -stacking in the multicomponent crystals of chloranilic acid, alkali hydrogenchloranilates, and water. *CrystEngComm* **2011**, 13, 4211–4217.

[27] Molčanov, K.; Kojić-Prodić, B. Face-to-face stacking of quinoid rings in crystals of alkali salts of bromanilic acid. *Acta Crystallogr.* **2012**, B68, 57–65.

[28] Molčanov, K.; Jelsch, C.; Wenger, E.; Stare, J.; Madsen, A. Ø.; Kojić-Prodić, B. Experimental evidence of 3-centre, 2-electron covalent bond character of the central O-H-O fragment on the Zundel cation in crystals of Zundel nitranilate tetrahydrate. *CrystEngComm* **2017**, 19, 3898–3901.

[29] Milašinović, V.; Molčanov, K. Nitranilic acid as a basis for construction of coordination polymers: from discrete monomers to 3D networks. *CrystEngComm* **2019**, 21, 2962–2969.

[30] Milašinović, V.; Molčanov, K. Alkali salts of nitranilic and cyanochloranilic acids. *Croat. Chem. Acta* **2018**, 91, 177–186.

[31] Molčanov, K.; Stare, J.; Kojić-Prodić, B.; Lecomte, C.; Dahaoui, S.; Jelsch, C.; Wenger, E.; Šantić A.; Zarychta, B. A polar/ π model of interactions explains face-to-face stacked quinoid rings: a case study of the crystal of potassium hydrogen chloranilate dehydrate. *CrystEngComm* **2015**, 17, 8645–8656.

- [32] Vuković, V.; Leduc, T.; Jelić-Matošević, Z.; Didierjean, C.; Favier, F.; Guillot, B.; Jelsch, C. A rush to explore protein-ligand electrostatic interaction energy with *Charger*. *Submitted for publication*, 2021.
- [33] Shahbazian, S. Why Bond Critical Points Are Not “Bond” Critical Points. *Chem. Eur. J.* **2018**, 24, 5401–5405.
- [34] Bader, R. F. W. Bond Paths Are Not Chemical Bonds. *J. Phys. Chem.* **2009**, A113, 10391–10396.
- [35] Wick, C. R.; Clark, T. On bond-critical points in QTAIM and weak interactions. *J. Mol. Model.* **2018**, 24, 142.
- [36] Xiang, J.; Chang, C.; Li, M.; Yuan, L.; Sun, J. A Novel Coordination Polymer as Positive Electrode Material for Lithium Ion Battery. *Cryst. Growth Des.* **2008**, 8, 280–282.
- [37] Bruker. SAINT. Bruker AXS Inc., Madison, Wisconsin, USA, 2012.
- [38] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, 42, 339–341.
- [39] Sheldrick, G. M. A short history of *SHELX*. *Acta Cryst.* **2008**, A64, 112–122.
- [40] Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, C71, 3–8.
- [41] Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *Mercury CSD 2.0* – new features for the visualization and investigation of crystal structures. *J. Appl. Crystallogr.* **2008**, 41, 466–470.
- [42] Persistence of Vision Pty. Ltd. Persistence of Vision™ Raytracer. Persistence of Vision Pty. Ltd., Williamstown, Australia, 2004. <http://www.povray.org/> (last access 2020-04-17).
- [43] Jelsch, C.; Guillot, B.; Lagoutte, A.; Lecomte, C. Advances in protein and small-molecule charge-density refinement methods using MoPro. *J. Appl. Crystallogr.* **2005**, 38, 38–54.

- [44] Blessing, R. H. An empirical correction for absorption anisotropy. *Acta Crystallogr.* **1995**, A51, 33–38.
- [45] Madsen, A. Ø. SHADE web server for estimation of hydrogen anisotropic displacement parameters. *J. Appl. Crystallogr.* **2006**, 39, 757–758.
- [46] Madsen, A. Ø.; Hoser, A. A. A simple approach to estimate isotropic displacement parameters for hydrogen atoms. *Acta Crystallogr.* **2015**, A71, 169–174.
- [47] Allen, F. H.; Bruno, I. J. Bond lengths in organic and metal-organic compounds revisited: X-H bond lengths from neutron diffraction data. *Acta Crystallogr.* **2010**, B66, 380–386.
- [48] Domagała, S.; Fournier, B.; Liebschner, D.; Guillot, B.; Jelsch, C. An improved experimental databank of transferable multipolar atom models - ELMAM2. Construction details and applications. *Acta Crystallogr.* **2012**, A68, 337–351.
- [49] Abrahams, S. C.; Keve, E. T. Normal probability plot analysis of error in measured and derived quantities and standard deviations. *Acta Crystallogr.* **1971**, A27, 157–165.
- [50] Zhurov, V. V.; Zhurova, E. A.; Pinkerton, A. A. Optimization and evaluation of data quality for charge density studies. *J. Appl. Crystallogr.* **2008**, 41, 340–349.
- [51] Meindl, K.; Henn, J. Foundations of residual-density analysis. *Acta Crystallogr.* **2008**, A64, 404–418.
- [52] Meindl., K. A. C. *Residual density validation and the structure of Labyrinthopeptin A2*, PhD Thesis. Mathematisch-Naturwissenschaftliche Fakultät, Georg-August-Universität Göttingen, October 2008.
- [53] Tang, W.; Sanville E.; Henkelman, G. A grid-based Bader analysis algorithm without lattice bias. *J. Phys. Condens. Matter* **2009**, 21, 084204.
- [54] Howard, S. T.; Lamarche, O. Description of covalent bond orders using the charge density topology. *J. Phys. Org. Chem.* **2003**, 16, 133–141.

- [55] Tsirelson, V. G.; Bartashevich, E. V.; Stash, A. I.; Potemkin, V. A. Determination of covalent bond orders and atomic valence indices using topological features of the experimental electron density. *Acta Crystallogr.* **2007**, B63, 142–150.
- [56] Bartashevich, E.; Nikulov, D.; Vener, M.; Tsirelson, V. QTAIME study of the X–H/H...O bond order indices (X=O, N, C) in molecular systems. *Comput. Theor. Chem.* **2011**, 973, 33–39.
- [57] Guillot, B.; Enrique, E.; Huder, L.; Jelsch, C. MoProViewer: a tool to study proteins from a charge density science perspective. *Acta Crystallogr.* **2014**, A70, C279.
- [58] Fournier, B.; Guillot, B.; Lecomte, C.; Escudero-Adán, E. C.; Jelsch, C. A Method to Estimate Statistical Errors of Properties Derived from Charge-Density Modelling. *Acta Crystallogr.* **2018**, A74, 170–183.
- [59] Kluyver, T.; Ragan-Kelley, B.; Pérez, F.; Granger, B.; Bussonnier, M.; Frederic, J.; Kelley, K.; Hamrick, J.; Grout, J.; Corlay, S.; Ivanov, P.; Avila, D.; Abdalla, S.; Willing, C.; Jupyter Development Team, „Jupyter Notebooks – a publishing format for reproducible computational workflows”. *Proceedings of the 20th International Conference on Electronic Publishing*. F. Loizides & B. Schmidt, eds. 2016.
- [60] Python Software Foundation, Python, 2001, <https://www.python.org/>. (Last access 2020-04-17).
- [61] McKinney, W. „Data Structures for Statistical Computing in Python”. *Proceedings of the 9th Python in Science Conference*. S. van der Walt & J. Millman, eds. 2010, pp. 51–56.
- [62] Dovesi, R.; Orlando, R.; Erba, A.; Zicovich-Wilson, C. M.; Civalleri, B.; Casassa, S.; Maschio, L.; Ferrabone, M.; De La Pierre, M.; D’Arco P.; Noël, Y.; Causà, M.; Rérat, M; Kirtman, B. CRYSTAL14: A program for the ab initio investigation of crystalline solids. *Int. J. Quantum Chem.* **2014**, 114, 1287–1317.
- [63] Dovesi, R.; Saunders, V. R.; Roetti, C.; Orlando, R.; Zicovich-Wilson, C. M.; Pascale, F.; Civalleri, B.; Doll, K.; Harrison, N. M.; Bush, I. J.; D’Arco, P.; Llunell, M.; Causà, M.; Noël, Y. *CRYSTAL14 User’s Manual*. Università di Torino, Torino, Italy, 2014.

[64] Gatti, C.; Saunders, V. R.; Roetti, C. Crystal field effects on the topological properties of the electron density in molecular crystals: The case of urea. *J. Chem. Phys.* **1994**, 101, 10686.

[65] Heyd, J.; Peralta, J. E.; Scuseria, G. E.; Martin, R. L. Energy band gaps and lattice parameters evaluated with the Heyd-Scuseria-Ernzerhof screened hybrid functional. *J. Chem. Phys.* **2005**, 123, 174101.

[66] Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. von R. Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21+G basis set for first-row elements, Li–F. *J. Comput. Chem.* **1983**, 4, 294–301.

[67] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2009.

[68] Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, 98, 5648–5652.

[69] Papajak, E.; Zheng, J.; Leverentz, H. R.; Truhlar, D. G. Perspectives on Basis Sets Beautiful: Seasonal Plantings of DiffuseBasis Functions. *J. Chem. Theory and Comput.* **2011**, 7, 3027–3034.

[70] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* **2010**, 132, 154104.

[71] Boys, S. F.; Bernardi, F. Calculation of Small Molecular Interactions by Differences of Separate Total Energies - Some Procedures with Reduced Errors. *Mol. Phys.*, **1970**, 19, 553.

[72] Yanai, T.; Tew, D.; Handy, N. A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, 393, 51–57.

Insert Table of Contents Graphic and Synopsis Here

The first case of a π -hole interaction involving a dianion as an acceptor was studied in detail by a combination of X-ray charge density and quantum chemical modelling. The total interaction is interpreted as a combination of an "inverse" π -hole interaction and chalcogen bonding and is dominantly of electrostatic nature.